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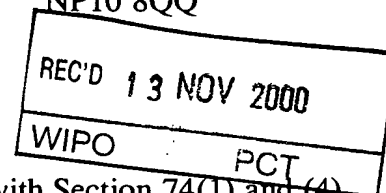
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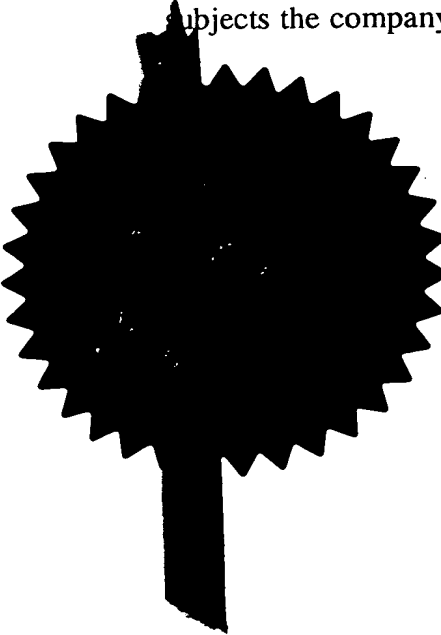


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1. Your reference

SMC 60399/GB/P

2. Patent
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Avecia Limited
Hexagon House
Blackley
Manchester, M9 8ZS

Patents ADP number (if you know it)

~~6254807002~~

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

77 641 37001

4. Title of the invention

Compounds

5. Name of your agent (if you have one)

MAYALL, John

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Avecia Limited
Hexagon House
PO Box 42
Blackley
Manchester M9 8ZS

6244 33003

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Number of earlier application

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Claim(s)

2

Abstract

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APPLICANTS

Avecia Limited

TITLE

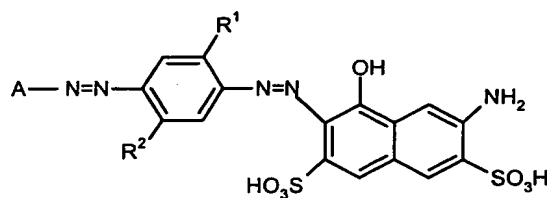
COMPOUNDS

COMPOUNDS

This invention relates to dyes, to inks and to their use in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

According to the present invention there is provided a compound of Formula (1) and salts thereof:



Formula (1)

wherein:

A is a substituted phenyl group carrying a group of the formula -NR³R⁴ and an ortho group selected from sulpho, phosphonato and phosphinato;

R¹ and R² are each independently optionally substituted alkyl or optionally substituted alkoxy;

R³ is H, optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl; and

R⁴ is an acyl group.

Preferred acyl groups represented by R⁴ are of the formula -COR⁵, -SOR⁵ or -SO₂R⁵, wherein R⁵ is H, optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl. It is especially preferred that R⁴ is of the formula CH₃(CH₂)_aCO- wherein a has a value from 0 to 3.

The optional substituents which may be present on R¹, R², R³ and R⁵ are preferably selected from -NH₂; halo, especially Cl, Br and F; ester, especially -CO₂-C₁₋₄-alkyl; -O-C₁₋₄-alkyl; -CO₂H; -SO₃H; -OR⁶; or -SR⁶; wherein each R⁶ independently is H or C₁₋₄-alkyl.

Preferably at least one of R¹ and R², or more preferably both R¹ and R², carries an -OH group.

When R^1 , R^2 , or R^3 is an optionally substituted alkyl group it is preferably an optionally substituted C_{1-4} -alkyl group, more preferably a C_{1-4} -alkyl group or a C_{1-4} -alkyl-OH group.

When R^1 or R^2 is an optionally substituted alkoxy group it is preferably an optionally substituted C_{1-4} -alkoxy group, more preferably a C_{1-4} -alkoxy group or a C_{1-4} -alkoxy-OH group.

When R^3 or R^5 is optionally substituted aryl it is preferably optionally substituted phenyl, more preferably phenyl or phenyl carrying a carboxy and/or sulpho group.

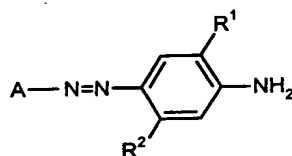
Preferably the ortho substituent is sulpho.

It is especially preferred that the group of formula $-NR^3R^4$ is in the para position with respect to the azo linkage because this gives particularly good high optical density.

R^1 and R^2 are preferably each independently optionally substituted C_{1-4} -alkyl or optionally substituted C_{1-4} -alkoxy, more preferably optionally substituted C_{1-4} -alkoxy, especially C_{1-4} -alkoxy-OH.

In one embodiment one of R^1 and R^2 is $-OC_{1-4}$ -alkyl-OH and the other is $-OC_{1-4}$ -alkyl or $-OC_{1-4}$ -alkyl-OH.

The dyes of Formula (1) may be prepared by diazotising a compound of the Formula (2) to give a diazonium salt and coupling the resultant diazonium salt with a 1-hydroxy-3,6-disulpho-7-aminonaphthalene:



Formula (2)

wherein A, R^1 and R^2 are as hereinbefore defined.

The hydroxy group(s) on R^1 and/or R^2 may be protected during the diazotisation, for example using an acid labile or base labile protecting group. The acetoxy protecting group is particularly convenient and inexpensive.

The diazotisation is preferably performed at room temperature or below. Preferably the diazotisation is performed in water, preferably at a pH below 7. Dilute mineral acid, e.g. HCl or H_2SO_4 , may be used to achieve the desired acidic conditions.

The compound of Formula (2) may be prepared by diazotising a compound of formula $A-NH_2$ and coupling onto an aniline compound carrying R^1 and R^2 groups at the 2- and 5- positions respectively, wherein A, R^1 and R^2 are as hereinbefore defined.

Preferred salts are alkali metal salts (especially lithium, sodium and potassium salts), ammonium and substituted ammonium salts and mixtures thereof. Especially

preferred salts are sodium, potassium and lithium salts, salts with ammonia and volatile amines and mixtures thereof. The lithium salts have good solubility, forming particularly storage stable inks with low tendency to block ink jet nozzles.

The dyes may be converted into a desired salt using known techniques. For example, an alkali metal salt of a dye may be converted into the ammonium or substituted ammonia salt by dissolving an alkali metal salt of the dye in water, acidifying with a mineral acid and adjusting the pH of the solution to pH 9 to 9.5 with ammonia or the amine and removing the alkali metal cations by dialysis or by use of an ion exchange resin.

Examples of amines which may be used to form such salts include methylamine, dimethylamine, trimethylamine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, iso-butylamine, sec-butylamine, tert-butylamine, piperidine, pyridine, morpholine, allylamine, diethylamine, triethylamine and mixtures thereof. It is not essential that the dyes are completely in the form of the ammonium salt or substituted ammonium salt and mixed alkali metal and either ammonium salt or substituted ammonium salt are effective, especially those in which at least 50% of the cations are ammonium or substituted ammonium ions.

Still further salts are those with the counter ions described in US 5,830,265, claim 1, integer (b), which are included herein by reference thereto.

The dyes of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present claims.

According to a second aspect of the present invention there is provided an ink comprising a compound of Formula (1) or salt thereof and a liquid medium or a low melting point solid medium.

A preferred ink comprises:

- (a) from 0.01 to 30 parts of a compound of the Formula (1) or salt thereof; and
- (b) from 70 to 99.99 parts of a liquid medium or a low melting point solid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a liquid, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates which may be used to prepare inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and polyalkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-soluble organic solvents.

Especially preferred water-soluble organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable ink media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the dye in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and storage stability of the ink.

Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

Preferred low melting solid media have a melting point in the range from 60°C to 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C₁₈₋₂₄ chains, and sulphonamides. The dye of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

The dyes of the invention may be used as the sole colorant in inks because of their attractive black shade. They benefit from particularly good light fastness, an attractive neutral black shade and good optical density. However, if desired, one may combine the dyes with one or more further colorants if a slightly different shade is required for a particular end use. The further colorants are preferably dyes. When further colorants are included in the ink these are preferably selected from black, cyan and yellow colorants and combinations thereof.

Preferred black colorants include C.I. Food Black 2, C.I. Direct Black 19, C.I. Reactive Black 31, PRO-JET Fast Black 2, C.I. Direct Black 195; C.I. Direct Black 168; and black dyes described in patents by Lexmark (e.g. EP 0 539,178 A2, Example 1, 2, 3, 4 and 5), Orient Chemicals (e.g. EP 0 347 803 A2, pages 5-6, azo dyes 3, 4, 5, 6, 7, 8, 12, 13, 14, 15 and 16) and Seiko Epson Corporation.

Preferred cyan colorants include C.I. Direct Blue 199; C.I. Acid Blue 9; C.I. Direct Blue 307; C.I. Reactive Blue 71; and C.I. Direct Blue 85.

Preferred yellow colorants include C.I. Direct Yellow 142; C.I. Direct Yellow 132; C.I. Direct Yellow 86; C.I. Direct Yellow 85; C.I. Direct Yellow 173; and C.I. Acid Yellow 23.

However, as mentioned above, it is not normally necessary to use further colorants in conjunction with dyes of the present invention.

The ink may also contain additional components conventionally used in ink jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, gellation reducing additives and surfactants which may be ionic or non-ionic.

A further aspect of the invention provides a process for printing an image on a substrate comprising applying an ink containing a dye of Formula (1) to the substrate by means of an ink jet printer.

The ink used in this process is preferably as defined in the second aspect of the present invention.

Preferably the ink contains less than 500ppm, more preferably less than 100ppm, especially less than 30ppm and more especially less than 20ppm in total of divalent and trivalent metal ions. The halide content is preferably less than 500ppm, more preferably less than 250ppm. The term 'ppm' means parts per million by weight based on the total weight of ink. The metal ion and halide content may be adjusted to the desired range using any suitable technique, e.g. ultrafiltration, reverse osmosis, ion exchange or a combination thereof.

The ink may be used 'as is' for ink jet printers or alternatively it may be used as a concentrate which is diluted and/or further formulated to give an ink jet printing ink. The concentrates are a useful form for transportation, avoiding the expense of transporting the water contained in finally formulated inks.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character.

Preferred paper are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available treated papers include HP Premium Coated Paper (available from Hewlett Packard Inc), HP Photopaper (available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film (available from Seiko Epson Corp.), Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper (available from Canon), Canon GP 201 and GP 301 Glossy Paper (available from Canon), and Canon HG 101 and HG201 High Gloss Film (available from Canon).

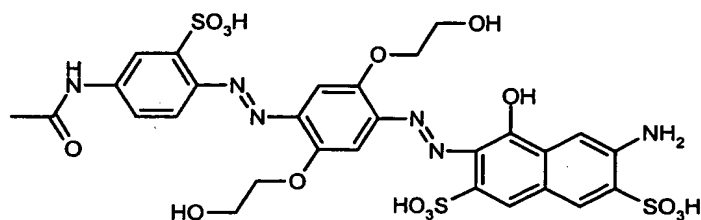
A further aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with an ink, a dye or by means of a process as hereinbefore defined.

A still further aspect of the present invention provides an ink jet printer cartridge, optionally refillable, comprising a chamber and an ink, wherein the ink is present in the chamber and the ink is as defined in the second aspect of the present invention.

The following examples illustrate how dyes according to the invention may be synthesised.

Example 1

Preparation of



Step 1

4-aminoacetanilide-3-sulphonic acid (17.7g) was dissolved in water (400ml) and the pH adjusted to 8-9 using lithium hydroxide (2M). The solution was carbon-screened and sodium nitrite (4.55g) added to the filtrate. The solution was then added to a mixture of ice and water to which had been added hydrochloric acid (20ml) and the mixture was stirred for 2hrs at 0-10°C. Excess nitrous acid was destroyed by the addition of sulphamic acid.

Step 2

2,5-bis(2-Acetoxyethoxy)aniline (17.82g) was dissolved in acetone (300ml).

Step 3- Coupling

The product from step 2 was added to the product from step 1. Pyridine (5ml) was then added and the mixture allowed to self warm before stirring for a further 16hrs at room temperature. The product was then filtered off and washed with lithium chloride solution (500ml, 10%), pulled dry on the filter and used without further purification.

Step 4

The product of step 3 was dissolved in water (500ml) by adjusting the pH to 10 using lithium hydroxide. The solution was screened and sodium nitrite (8.28g) added to the filtrate. The mixture was then added to a stirred solution of hydrochloric acid (20ml) in water (100ml) and stirred for 1.5hrs at room temperature before destroying excess nitrous acid using sulphamic acid.

2R acid (22.26g) was dissolved in water (300ml) by adjusting the pH to 10 using lithium hydroxide solution (2M). The solution was stirred at 0-10°C and the diazonium salt

5 solution added slowly maintaining the pH at 10-10.5 throughout the addition. On completion of the addition the mixture was further stirred for 1hr at 0-10°C. The product was isolated by filtration and washed with lithium chloride solution (1l, 30%). The damp cake was slurried in acetone (1l) using a high shear mixer, filtered and washed with acetone.

Step 5- Preparation of the Title Product

10 The product from Step 4 above was dissolved in water (1l) and lithium hydroxide (40g) added. The solution was stirred at 20°C until thin layer chromatography showed the hydrolysis to be complete (approximately 2 hours). The pH was adjusted to 8. Lithium chloride (25% w/v) was then added slowly and the product isolated (hot) by filtration and washed with lithium chloride (1l, 30%). The resultant product was dissolved in water (500 ml) and purified by dialysis. Evaporation of the water at 70°C gave the title product (12.59g) in the form of its lithium salt having a lambda max. at 598nm.

15 Example 2-12 - Mixtures

The dye mixtures described in Table A may be prepared in which all parts are by weight and are shown in brackets. CID means C.I. Direct and CIA means C.I. Acid.

TABLE A

Example	2	3	4	5	6	7	8	9	10	11	12
Dye from Example No.	1(80)	1(90)	1(60)	1(75)	1(95)	1(92)	1(89)	1(81)	1(60)	1(77)	1(79)
CID Yellow 132	10			2			4			7	
CID Yellow 142		10		5						6	
CID Yellow 86				5						10	
CIA Yellow 23			10								
CIA Blue 9					5						
CIA Blue 307				3		8					
CID Black 168							11				
CI Food Black 2	10								20		
CID Black 19			30	10				15	20		
CID Yellow 173											21

5

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Inks

The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the Dye or mixture made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrrolidone

MIBK = methylisobutyl ketone

P12 = propane-1,2-diol

BDL = butane-2,3-diol

CET= cetyl ammonium bromide

PHO = Na_2HPO_4 and

TBT = tertiary butanol

TDG = thiodiglycol

TABLE I

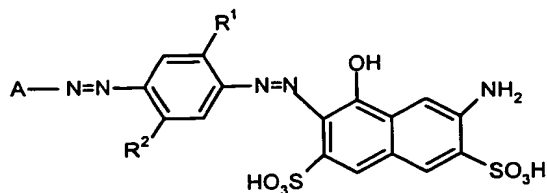
Dye/ Mixture	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.	85	3		3	3				5	1	
4	1.1	81			9		0.5				9	
5	2.5	60	4	15	3	3			6	10	5	4
6	5	65		20					10			

TABLE II

Dye/ Mixture	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
7	3.0	80	15			0.2					5	
8	9.0	90		5						1.2		5
9	1.5	85	5	5		0.15	5.0	0.2		0.12		
10	2.5	90		6	4							
11	3.1	82	4	8		0.3			5			6
12	0.9	85		10						0.2		

CLAIMS

1. A compound of Formula (1) and salts thereof:



Formula (1)

wherein:

A is a substituted phenyl group carrying a group of the formula -NR³R⁴ and an ortho group selected from sulpho, phosphonato and phosphinato;

R¹ and R² are each independently optionally substituted alkyl or optionally substituted alkoxy;

R³ is H, optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl; and

R⁴ is an acyl group.

2. A compound according to claim 1 wherein at least one of R¹ and R² carries an -OH group.

3. A compound according to any of the preceding claims wherein R³ is selected from optionally substituted C₁₋₄-alkyl and optionally substituted phenyl.

4. A compound according to any of the preceding claims wherein R³ is selected from C₁₋₄-alkyl, C₁₋₄-alkyl-OH, phenyl and phenyl carrying a carboxy and/or sulpho group.

5. A compound according to any of the preceding claims wherein R⁴ is of the formula -COR⁵, -SOR⁵ or -SO₂R⁵, wherein R⁵ is H, optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl.

6. A compound according to any of the preceding claims wherein R⁴ is of the formula CH₃(CH₂)_aCO- wherein a has a value from 0 to 3.

7. A compound according to any of the preceding claims wherein the ortho group is sulpho.

8. A compound according to any of the preceding claims wherein the group of the formula $-NR^3R^4$ is in the para position with respect to the azo linkage.

9. A compound according to any one of the preceding claims wherein R^1 and R^2 are each independently optionally substituted C_{1-4} -alkyl or optionally substituted C_{1-4} -alkoxy, provided that at least one of R^1 and R^2 carries an -OH group.

10. A compound according to any one of the preceding claims wherein R^1 and R^2 are each independently C_{1-4} -alkoxy-OH.

11. A compound according to any one of the preceding claims wherein both R^1 and R^2 carry on -OH group.

12. A compound according to any one of the preceding claims wherein one of R^1 and R^2 is $-OC_{1-4}$ -alkyl-OH and the other is $-OC_{1-4}$ -alkyl or $-O-C_{1-4}$ -alkyl-OH.

13. An ink comprising a compound according to any one of the preceding claims and a liquid medium or a low melting point solid medium.

14. An ink according to claim 13 which contains a further colorant selected from black, cyan and yellow colorants.

15. An ink according to claim 14 or 15 which contains less than 500ppm in total of divalent and trivalent metal ions.

16. A process for forming an image on a substrate comprising applying and ink according to claim 13, 14 or 15 to the substrate by means of an ink jet printer.

17. A paper, an overhead projector slide or a textile material printed with an ink according to claim 13, 14 or 15, a compound according to any one of claims 1 to 12 or by means of a process according to claim 16.

18. An ink jet printer cartridge, optionally refillable, comprising a chamber and an ink, wherein the ink is present in the chamber and the ink is as defined in claim 13, 14 or 15.